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DENSITY FUNCTIONAL CALCULATIONS FOR PREDICTION OF ULTRA-THIN FILM STRUCTURE AND PROPERTIES

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ABSTRACT

Most of the published theoretical and calculational effort on unsupported, ordered, ultra-thin films ("UTF") in vacuo has focused on the thickest computationally feasible systems as models for surface properties of semi-infinite slabs. Crystalline periodic length scales in two cartesian dimensions combined with molecular-scale thickness in the third, however, make UTF's strong candidates for the occurrence of quantum interference effects. Many UTF properties were predicted first from jellium slab models. A noteworthy prediction was that there would be large oscillations in the work function as a function of layer number. Extensive calculations on a variety of N-layers ($N = 1, 2, 3, \dots$ atomic planes) using all-electron, full-potential, local-spin-density approximation techniques show that the work function oscillation is weaker than expected but that there are significant layer-number dependences in the equilibrium lattice parameters, inter-planar spacings, electronic structure, density of states, and electronic stopping power. This paper reviews our own calculations as well as some others. Our objectives include the discernment of systematics within UTF's, systematics in relationship to their counterpart crystals, relationship with surface properties, and appraisal of challenges to current models and methods.

1. Motivation and Objectives

Modelling the surface of a semi-infinite crystal by a slab which is translationally periodic parallel to its faces has been a commonplace for many years. One of the computational resources challenges for such studies is the problem of “the thicker the better.” Enough layers must be included to reduce both surface-surface interactions and interior relaxations (relative to the infinite crystal) to negligibility. Both supercell (periodic replication of the slab) and free slab (vacuum boundary conditions) calculations are done.

Viewed from a different perspective, the free slabs motivate a distinct (though not entirely separate) set of questions, even though the formal techniques and implementing algorithms for treating the free slabs are indistinguishable in the two cases. The alternative perspective arises from recognition of the technological rush to reduce micro-electronic feature size. For layered systems that trend means inexorable reductions in thickness. In contrast to modelling of semi-infinite slabs, the technological asymptote of the world of micro-electronics is “the thinner the better.” A slab which is thin on the scale of several molecular bond lengths yet retains crystalline periodicity and length scales parallel to its faces, is, however, a strong candidate for the occurrence of quantum interference effects. In addition to their intrinsic interest, such static quantum size effects could have profound implications (desirable or undesirable) for whatever technological objectives dictated thinness in the first place.

Ultra-thin films (UTF's) also are of interest because they are mesoscopic structures which correspond to the ordered system limit analogous with separated atoms (the “delamination limit”). By construction such systems have little in the way of an interior, hence their structure and properties may be different from the surface properties induced in a cleaved crystal. Some of those properties, notably UTF response to charged particle irradiation and to overlayer deposition, are matters of intense practical interest as regards the development of advanced micro-electronic fabrication techniques.

Unsupported UTF's are not yet an experimental reality. That being the case, the value of chemically specific first principles calculational studies is to predict trends and relationships amongst systems not yet made but right over the experimental horizon and to relate those trends to known systems, e.g. bulk crystals and their surfaces.

The significance of chemical specificity is illustrated by the original prediction of a UTF static quantum size effect (SQSE). Nearly two decades ago Schulte¹ showed that the jellium model UTF produced oscillations in the work function as a function of thickness of order 0.5 – 1.0 eV (see Fig. 8 of Ref. 1). Elaboration followed² with an important point being that geometric relaxation might reduce but not suppress the effect. In the interim a set of systematic treatments of thickness dependencies in Al fcc (111) UTF's^{3,4} showed clearly that SQSE's could be found in a system with realistic electrons, nuclei, and periodicities. (Only much later was an alkali metal sequence of UTF's studied; we return to this point below.)

It was also found, however, that growth on a supposedly inert substrate would suppress the effect.^{3(b)} That calculation illustrated, however, the essential need for reliable prediction of trends in the behavior of both unsupported UTF's and heterogeneous layered assemblies of them. SQSE's are, moreover, but one aspect of the more general question of systematic dependencies

of system properties upon the number of atomic layers. Such dependencies, beginning with structural parameters themselves, are affected strongly by system chemistry.

2. Effect of Objectives on Methodology

As presented in the original papers,^{5,6} we use Density Functional Theory⁷ and solve the Kohn-Sham equations in a basis of gaussian orbitals. To accelerate the calculation, four-center integrals are eliminated by use of an auxiliary basis of gaussians to expand the density, with the expansion coefficients determined by minimization of the Coulomb energy error resulting from the fit. The energy densities which depend non-linearly on the electron density that are ubiquitous in DFT also are expanded in an auxiliary gaussian basis with the coefficients determined by least squares on a numerical integration sampling grid. Taken together one gets a contribution to the alphabet soup of methodological nomenclature: our method is LCGTO-FF (Linear Combination of Gaussian Type Orbitals with Fitting Functions).

The focus on prediction of trends in UTF structures and properties and their relationship to bulk crystals and cleaved surfaces has multiple effects on the choice of methodology. First, we choose DFT because it is the overwhelming favorite for first principles study of solids and their cleaved surfaces. (Until recently this choice meant that there were relatively few molecular calculations with which to compare but the recent burst of interest in DFT in the quantum chemistry community is changing that.)

Second, we do not use relativistic corrections. The systems considered are all relatively light. In addition, there is a real problem of understanding the behavior of such corrections in the context of approximations made to implement DFT (see discussion of Table I) as well as the more fundamental question of what it means to combine the Dirac and HKS Hamiltonians.

Third, we still use the local (spin) density approximation [L(S)DA] not the generalized gradient approximations (GGA) which have been a focus of much attention in the DFT community for the last few years. In essence the issue is "mas vale lo malo conocido que lo bueno por conocer" ("better the known evil than the as yet unknown good"). GGA's are fascinating from the perspective of developing DFT to its full potential but they are not yet "ready for prime time" in regards to materials physics.

To support this critique, consider the task of predicting the ground state of crystalline Al. Table I summarizes all the modern LDA and GGA calculations. One set, by Juan and Kaxiras (ref. "h" in the Table), is sufficiently anomalous as to lattice constant and binding energy that we drop it from consideration. Several observations can be made. For the NON-relativistic calculations, reasonable LDA's do not give shortened bonds in spite of overbinding. This behavior is distinct from findings in molecules. Also notice that the very simplest LDA, KSG (i.e. $X\alpha$ with $\alpha = 2/3$), does *not* overbind, contrary to its behavior in molecules. For the LDA, the relativistic calculations all clump at $a_0 = 7.52 - 7.54$ au while all the non-relativistic ones clump at 7.58 - 7.60 (except for the KSG LDA which gives a consistent, larger value). Similarly the nonrelativistic B 's are all ≤ 80 GPa, while the relativistic values are all > 82 GPa. The choice of LDA does not seem to affect the behavior of the relativistic calculations: bonds are short and E_c is too negative (but no more so than the non-relativistic calculations). Turning to the GGA, there is no clear pattern to E_c ; the few reports do show remarkable disparity. The

PW91 GGA seems to be less sensitive to the relativistic bond shortening than the LDA if one compares the Garcia et al., Juan et al., and Dufek et al. calculations. The Khein et al. PW91

Reference	Relativity; LDA or GGA; pseudopotential?	$-E_c$ (eV/atom)	a_c (a.u.)	B (GPa)
Expt (a,b,c)		3.37	7.60	72.7
B & T (d)	NR; HL; no	4.07	7.60	79.7
L & C (e)	NR;Wigner; yes	3.65	7.58	71.5
M, J, & W (f)	NR; HL; no	3.88	7.60	80
B & T (g)	NR; KSG; no	3.20	7.65	96.8
J & K (h)	NR; PZ; yes	4.14	7.43	87.65
K, S & U (i)	FR/SR; PW; no	4.16	7.52	83.9
D, B, & S (j)	SR; HL; no	—	7.54	84
S et al. (k)	SR; HL; no	4.01	7.54	82.2
G. et al. (l)	SR; PZ; yes	4.05	7.48	87
J&K (h)	NR; PW91; yes	3.22	8.03	61.1
J, K, & G (m)	NR; PW91; yes	3.45	7.62	79.3
D, B, & S (j)	SR; EV; no	—	7.91	55
D, B, & S (j)	SR; PW91; no	—	7.65	74
K, S, & U (i)	FR/SR; PW91; no	3.74	7.74	72.6
G. et al. (l)	SR; BP; yes	3.23	7.65	77
G. et al. (l)	SR; PW91?; yes	3.09	7.63	79

Table I. Calculated results for the Crystalline Al Ground State (fcc). The column "Relativity" indicates whether the calculation was non-relativistic (NR), scalar-relativistic (SR) or fully relativistic (FR); a slash separates core from valence. The various exchange-correlation models are HL = Hedin-Lundqvist, KSG = Kohn-Sham-Gaspar ($X\alpha$ $n=2/3$), Wigner = KSG plus Wigner correlation formula, PZ = Perdew-Zunger, PW91 = Perdew-Wang (1991 version), BP= Becke-Perdew, EV= Engel-Vosko. GGA's are below the double line. E_c is the static lattice cohesive energy, a_c the equilibrium lattice constant, and B the bulk modulus. Notes: (a) Lattice constant extrapolated to $T = 0$ according to Ref. (e) below; (b) Bulk modulus according to Ref. 9; (c) E_c for static lattice per ref. (g) below; (d) Ref. 8; (e) P.K. Lam and M.L. Cohen, Phys. Rev. B 24, 4224 (1981); (f) V.L. Moruzzi, J.F. Janak, and A.R. Williams *Calculated Electronic Properties of Metals* (Pergamon, NY, 1978); (g) J.C. Boettger and S.B. Trickey, Phys. Rev. B 29, 6434, (1984); (h) Y-M Juan and Γ Kaxiras, Phys. Rev. B 48, 14944 (1994); (i) A. Khein, D.J. Singh, and C.J. Umrigar, Phys. Rev. B 51, 4105 (1995); (j) P. Dufek, P. Blaha, and K.Schwarz, Phys. Rev. B 50, 7279 (1994); (k) M. Sluiter, G. De Fontaine, X.Q. Guo, R. Podloucky, and A.J. Freeman, Phys. Rev. B 42, 10460 (1990); (l) A. Garcia, C. Elsässer, J. Zhu, S.G. Louie, and M.L. Cohen, Phys. Rev. B 46, 9829 (1992); 47 4150(E) (1993) [This may be a PW86 calculation]; (m) Y-M. Juan, E. Kaxiras, and R.G. Gordon, Phys. Rev. B 51, 9521 (1995)

calculation differs by being dramatically longer in bond than the presumably equivalent FLAPW calculation of Dufek et al.. The difference may be in the way the FLAPW sphere boundary discontinuity in the GGA potential was treated or in the use of fully relativistic cores by Khein et al. Ostensibly the same GGA, PW91, gives a slightly shorter bond in the non-relativistic, pseudo-potential calculation (including core-valence corrections) of Juan, Kaxiras, and Gordon, but 0.3 eV/atom less binding and a nearly 10% higher value of B .

What is curious about this table from the point of view predicting materials systems trends is that the GGA's are no better at predicting bond lengths than the LDA and, if anything, are worse at bulk moduli. What's more, our recent LDA calculation of the Al phase transitions⁸ agrees quite well with the most recent experimental data to above 200 GPa.⁹ Because of the range of disparate results for the same GGA, one suspects that technical and implementation subtleties are involved. Rather than risk suggesting trends to experimenters on the grounds of such subtleties, we choose the LSDA. At least its limitations are well-explored and documented.

The motivation for using all-electron calculations is simpler. Implicitly the rationale for pseudopotentials is that chemistry and materials physics takes place in the valence shells. True enough, but core-valence orthogonality is more than just a theorist's technical issue. Because of it, phenomena in the valence manifold can be probed by measuring response in the core. Surface core-level shifts are one example. Proton stopping power is another.

Gaussian orbital methodology has two motivations. The technical ground for the choice is the rich array of numerically potent techniques for evaluating the required matrix elements. The conceptual ground is, first, the facilitation of direct connection and intercomparison with molecular calculations, for which gaussian orbitals are *de rigueur*. At a deeper level, the conceptual ground might be called the Slater doctrine: the electron densities of molecules, polymers, films, and crystals are much closer to being those of perturbed atoms than of perturbed free particles, hence localized functions which one can integrate (gaussians) are preferable *a priori* to diffuse functions one can integrate (plane waves). We have checked our codes against whatever other full-potential, all-electron UTF calculations were available. A set of 1-L calculations we have found particularly useful is by Wimmer.¹⁰

3. Systems and Findings

Size effects in Li and Al UTF's

Relaxed (i.e. geometry optimized) Li UTF's with $1 \leq N \leq 5$ were treated in Ref. 11. The surface energies E_s in that paper are incorrect; see Ref. 12. No prior or subsequent calculations (except for our own and the 1-L study in Ref. 10) are available for comparison to our knowledge. Unrelaxed Al UTF's for $1 \leq N \leq 7$ were treated in Ref. 13; prior works for comparison are the aforementioned Refs. 3 and 4.

Table II summarizes the most interesting structural parameters, the work function, and the Density of States (DOS), $N(\epsilon)$, at the Fermi level for the Li UTF sequence. The system geometry is hcp (0001); the experimental data correspond to the 9K close-packed structure. The UTF surface energies are from Ref. 12, not 11. The crystalline data shown are from an FLAPW calculation¹⁴ (which used the same LDA) except for E_F , which is as calculated in Ref. 12, and

E_s , which is an experimental value cited there. Comparison with calculated crystalline energetics and structural parameters, not experimental ones, is essential to discern trends because of the need to avoid or reduce as much as possible the effect of systematic errors in LSDA relative to experiment.

N	$-E_c$	E_s	φ	$N(E_F)$	a_e	d_{int}	d_{ext}
1	1.10	0.255	3.56	0.49	5.73	—	—
2	1.39	0.220	3.63	0.55	5.76	—	4.27
3	1.48	0.195	3.60	0.58	5.75	—	4.39
4	1.51	0.200	3.61	0.46	5.69	4.38	4.32
5	1.53	0.200	3.56	0.47	5.67	4.37	4.41
Crystal	1.61	0.26	—	—	5.65	4.64	4.64

Table II Cohesive energy, surface energy (both in eV/atom), work function (eV), density of states at the Fermi level (states/eV-atom), equilibrium intraplanar lattice parameter, equilibrium interior interplanar lattice parameter, and equilibrium exterior one (all in au), all for Li UTF's. See text for sources.

From the tabulated results it is clear that if there is a work function SQSE in Li UTF's it is extremely small. It is doubtful that the calculations are precise enough to claim such a result. In marked contrast, there is a strong SQSE in $N(E_F)$. That variation is suppressed severely if the system is kept at ideal crystalline lattice parameters.

Even more striking is a *qualitative* SQSE in $N(\epsilon)$ which cannot be seen from the Table, namely one nearly square-wave step upward per layer below E_F . (For the sake of space, the DOS plots are not reproduced here; see Ref. 11). That behavior follows directly from the square-wave DOS associated with parabolic bands in systems with 2-D translational symmetry. For the Li UTF's the occupied (wholly or partly) bands are very nearly parabolic, hence each increase in N by unity adds one nearly square step to the DOS below E_F . This qualitative behavior, a one-to-one correspondence between a set of DOS features and N should be a directly testable prediction.

The Li UTF structural parameters also exhibit layer-number dependence. In particular, by $N = 5$, the interplanar lattice parameter, a_e , has settled to a value very close to that for crystalline hcp Li. The interplanar parameters d_{int} , d_{ext} (respectively the value of the hcp $c/2$ between planes not adjacent to the surface and the value separating the two planes at and next to the surface) are very different from crystalline values, with a small but clearly discernible even-odd oscillation in d_{ext} . Neither interplanar spacing is anywhere near the crystalline $c/2$ even at $N = 5$. The oscillatory behavior makes estimation of the number of layers needed to reach bulk-like behavior quite difficult. On energetic grounds, we estimated between 17 and 33, depending on the criterion used. The essential point is independent of the precise numerical value: UTF's are distinct from thick slabs excised from crystals.

Table III gives the energetic parameters for the Al fcc (111) UTF's; for brevity we restrict the tabulation to $1 \leq N \leq 6$, the systems for which our calculations¹³ using a dense (37 point) BZ mesh were done. (Ref. 13 also has results through $N = 7$ on a 19 point mesh; the overall trends are not different.) Note should be taken that Ref. 3(b) used the Wigner LSDA, Ref. 4 used the Perdew-Zunger form, while we used Hedin-Lundqvist. The differences between the sequences of work functions are caused primarily by the different LSDA's. Note also that Ref. 4 used a repeated slab approximation, while Ref. 3(b) used only a 10-point BZ scan.

N	$-E_c$	E_s	$E_s^{(a)}$	$E_s^{(b)}$	φ	$\varphi^{(a)}$	$\varphi^{(b)}$
1	3.078	0.506	0.40	0.47	4.873	4.74	4.3
2	3.605	0.486	0.18	—	4.636	4.53	—
3	3.787	0.454	0.39	0.50	4.372	4.10	3.2
4	3.831	0.519	0.48	—	4.323	4.43	—
5	3.880	0.526	—	0.49	4.553	4.34	3.4
6	3.915	0.526	0.52	—	4.482	4.31	—

Table III Cohesive energy, surface energy (both in eV/atom), and work function (eV) for Al UTF's. Unsuperscripted quantities ours; (a) Ref. 3(b); (b) Ref. (4).

What one sees is a marked size effect in $E_s(N)$, which declines through $N = 3$, then jumps up for the 4-L, the first in the sequence with a genuine interior volume. The work function behaves similarly but has the jump between $N = 4$ and 5, namely at the occurrence of the first system with a genuine interior *plane*. Ref. 3(b) puts the jump in φ between $N = 3$ and 4; the relative coarseness in their BZ scan density could easily be the source of this discrepancy.

Photoelectron spectra for rather thick (from our perspective) Al films, about 500 layers, have been published recently.¹⁵ The main features (Ref. 15, Fig. 2) are maxima at about 3 eV and 7 eV below E_F . Ref. 13 did not include the calculated DOS but the data are available. For the 7-L UTF, the DOS has maxima at 5.9 and 8.9 eV below E_F . There is a rounder, lower maximum right at E_F . The calculated bulk DOS¹⁶ has similar features at about -0.5 eV and -2.5 eV. In view of the different thicknesses, different methods, and known limitations on the interpretation of bare Kohn-Sham eigenvalues, the agreement among experiment and the two calculational limits seems reasonable.

The N -dependence of the cohesive energies is discussed in the next sub-section. We conclude this sub-section by summarizing. Even though an alkali metal is supposedly most nearly free-electron-like, the Li UTF's do not exhibit the work function oscillations predicted from a jellium slab model. By contrast, the Al (111) UTF work function sequence is confirmed to have a strong quantum size effect, of the same order of magnitude as predicted by the jellium model. The striking size effect in the Li UTF's is the step function DOS which is correlated one-to-one with the number of layers and the related strong layer-number dependence in $N(E_F)$.

Stopping, Surface Energies, and 1/N Dependences

A key quantity for understanding the fundamentals of ion implantation, radiation hardness, and similar phenomena in UTF's is the proton stopping power. The linear energy loss, $-\frac{dE}{dx}$, of a swift ion in matter generally is expressed as

$$-\frac{1}{n} \frac{dE}{dx} = S(\vec{v}) = \frac{4\pi Z_1^2 Z_2 e^4}{mv^2} L(\vec{v}) \quad (1)$$

where S , L are the stopping cross section and stopping number per scatterer, respectively, n is the number density of scatterers, \vec{v} the velocity of the incident particle, E its energy, x its path length, Z_1 the projectile charge, and Z_2 the number of electrons per target atom. The effects of channelling and changes in projectile charge state are neglected.

For a large but finite sample composed of N atomic layers, the stopping cross section can be expanded in a power series in $1/N$ about the infinite crystal case,¹⁵ yielding (at specified velocity)

$$S(1/N, v) = S(0, v) + \sum_j \frac{N^{-j}}{j!} \frac{\partial^j S}{\partial (1/N)^j} \Big|_{N=\infty} \quad (2)$$

The correction terms account for surface effects and structural differences between the crystal and the N -layer. Because the calculated $S(1, v)$ in general differs substantially from the crystalline value $S(0, v)$ (most notably near the stopping peak, $v = v_{max}$), terms in $1/N$ clearly sum to a significant correction for small N .

For large N the leading terms in eq. 2 are $S(1/N, v) = S(0, v) + \frac{1}{N} S_{surf}(v)$ with $S_{surf}(v)$ the leading surface contribution. For UTF's the opposite limit, the case of small N , is relevant. Curiously, when we examined¹⁷ our calculated values of $S(N, v)$ they also exhibited a linear dependence upon $1/N$ in this very different regime of layer number. The constant coefficient is reasonably consistent with the crystalline stopping cross section determined independently.

The inputs were previously published stopping cross sections for fully relaxed Li,^{18(a)} unrelaxed diamond,^{18(b)} and relaxed graphite^{18(b)} N -layers. [Computational methods and prior references are in Refs. 19. The methodology is a local density approximation to the orbital mean excitation energies which are the materials-specific parameters in the Oddershede-Sabin generalization of kinetic theory of stopping, itself a form of Bethe theory.] Fits to

$$S(1/N, v) = S(0, v) + \frac{1}{N} S_L(v) \quad (3)$$

yield the parameters found in Tables IV and V. The graphite results are so flat that only $N = 1, 2$ are needed. The other two systems have $1 \leq N \leq 4$. The projectile velocities were selected to be above the stopping maximum, in the velocity regime where the underlying theory should hold. All the fits are within the estimated precision of the calculations, with the small variations readily attributable to minor computational artifacts (e.g. numerical integration meshes) which have slightly different effects for differing numbers of layers. For velocities in the vicinity of the stopping maximum, the fitted $S(0, v)$ values are uniformly but modestly higher (10–15%) than either experimental or theoretical determinations of $S_{crystal}(v)$. The discrepancy between them is small if one takes into account the significant qualitative differences between the determination

of $S_{crystal}(v)$ and the N -Layer calculations on which the fits were based. For example the Li results would need error bars of only $\pm 6\%$ on each of the two values (crystal, fitted) to bring them within coincidence.

v (a.u.)	diamond		graphite	
	$S_L(v)$	$S(0, v)$	$S_L(v)$	$S(0, v)$
2.00	5.03	12.00	-0.02	12.75
2.50	2.95	11.57	—	—
3.00	1.91	10.31	—	—
5.00	0.74	6.00	—	—
6.63	0.41	4.26	0.00	4.29

Table IV Fitted slope and intercept for stopping cross section (cross section units are 10^{15} eV cm²/atom) in unrelaxed diamond ($N = 1-4$) and relaxed graphite UTF's ($N = 1,2$).

v (a.u.)	$S_L(v)$	$S(0, v)$
1.25	2.32	13.00
1.50	1.52	11.69
1.75	1.11	10.53
2.50	0.53	7.95
4.00	0.21	5.05
6.00	0.09	3.02

Table V As in preceding table for relaxed Li UTF's ($N=1-4$).

Rationalization of the linear $1/N$ dependence at small N on the basis of the Bragg rule

$$\begin{aligned}
 S(N, v) &= \frac{1}{N} [N S(1, v) + S_{interaction}(v)] \\
 &= S(1, v) + \frac{1}{N} S_{interaction}(v)
 \end{aligned} \tag{4}$$

clearly will not work. The 1-L rather than the crystal is the Bragg rule asymptote. Said another way, the Bragg rule is a weak binding approximation yet weak binding is not a common characteristic for all three systems. Different physics is involved. The connection is with surface energy calculations.^{12, 20}

Gay et al. pointed out²⁰ that, for a sufficiently thick N -layer, the cohesive energy per slab unit cell $E_{c,cell}(N)$, the crystalline cohesive energy $E_{c,crystal}$, and the surface energy E_s are related by

$$E_{c,cell}(N) = N E_{c,crystal} + 2 E_s \tag{5}$$

Obviously the N -layer cohesive energy $E_c(N)$ (for a monatomic surface unit cell) follows:

$$E_c(N) \equiv (1/N)E_{c,cell}(N) = E_{c,crystal} + 2E_s/N \quad (6)$$

Since eq. 6 is for large, finite N , the small N relaxation effects may be written in the same way as in eq. 2

$$E_c(N) = \sum_{j=0}^{\infty} N^{-j} \mathcal{E}_j \quad (7)$$

with

$$E_{c,crystal} = \lim_{N \rightarrow \infty} E_c(N) = \mathcal{E}_0 \quad (8)$$

and $E_s = \mathcal{E}_1/2$ for sufficiently large but finite N as before.

If either the relaxation effects leave the N -layer cohesive energies unshifted with respect to the unrelaxed N -layer values, or the UTF's are treated at crystalline geometries, the linear approximation to Eq. 7 should fit the calculated values. The systems studied happen to fit these criteria. Details are in Ref. 17; here we summarize.

The relaxed and unrelaxed cohesive energies of the Li 1- through 5-Layers differ at most by 0.01 eV/atom. (As noted above, the Li N -layer *geometries* have significant relaxation effects: the distinction is consistent with the small bulk modulus of Li.) The Li N -layer cohesive energies fit very nicely to

$$E_c(N) \approx \mathcal{E}_0 + \frac{1}{N} \mathcal{E}_1 \quad (9)$$

with $\mathcal{E}_0 = -1.67$ eV/atom, $\mathcal{E}_1 = 0.57$ eV, values in excellent agreement with the measured values of $E_{c,crystal}$ and $2E_s$ respectively.¹²

The unpublished cohesive energies for the unrelaxed diamond give $\mathcal{E}_0 = -8.385$ eV/atom, $\mathcal{E}_1 = 6.495$ eV. Since the system has highly unphysical unreconstructed surfaces, \mathcal{E}_1 is also unphysical as a surface energy. However, \mathcal{E}_0 exhibits excessive binding completely consistent with the overbound $E_{c,crystal}$ found by Chelikowsky and Louie's bulk diamond calculation²¹ using the same LDA: $E_{c,crystal} = -8.02$ eV/atom. The 0.35 eV/atom discrepancy between the two is not surprising. Because the N -layer calculations were for an unphysical system (no surface reconstruction in a C film), they were unoptimized with regard to fitting function basis sets. An odd technical characteristic of the LCGTO-FF method is that an unoptimized charge fitting basis causes spurious extra binding.

Cohesive energies, but not stopping cross sections, also are available for unrelaxed 1-6 layers of Al; see Table III above and Ref. 13. Those energies fit almost perfectly with $\mathcal{E}_0 = -4.08$ eV/atom, $\mathcal{E}_1 = 1.00$ eV. The former value is exactly the crystalline cohesive energy found in our recent LCGTO-FF calculation which used the same LDA,⁸ while the latter value is twice the published experimental surface energy.¹³

The extremely high quality of predicted values of $E_s = \mathcal{E}_1/2$ suggests a simple extension of the reasoning of Ref. 12. There it is argued that the incremental energy (the difference in cohesive energy per film cell)

$$\begin{aligned} E_{inc}(N) &= E_c^{cell}(N) - E_c^{cell}(N-1) \\ &= NE_c(N) - (N-1)E_c(N-1) \end{aligned} \quad (10)$$

is the best consistent estimator (in the sense of avoiding inter-calculation accumulation of error) of the crystalline binding energy obtainable from a series of UTF calculations. Analytically that argument amounts to beginning with Eq. 8, then forming

$$E_{inc}(N) = N \sum_{j=0}^{\infty} N^{-j} \mathcal{E}_j - \sum_{l=0}^{\infty} (N-1)^{-l} \mathcal{E}_l \quad (11)$$

For $N \geq 3$ (because at least three points are necessary to determine the coefficients), the leading terms are

$$\begin{aligned} E_{inc}(N) &\approx \mathcal{E}_0 - \frac{1}{N(N-1)} \mathcal{E}_2 \\ &\approx E_{c,crystal} \end{aligned} \quad (12)$$

Thus it appears that calculation of E_s by the latter approximation¹² could be improved by use of the fitted \mathcal{E}_0 , especially for those UTF sequences which have a significant non-linearity of cohesive energy in $1/N$.

To conclude this section, we return to the physics of the linear scaling of the proton stopping cross section with $1/N$. E_c is calculated in the adiabatic approximation, hence reflects the behavior of the target electron population alone. For all the systems studied, E_c varies linearly with $1/N$. Electronic stopping is determined by electron excitation, hence the more bound the system per atom (for a specified chemical species and symmetry; see Ref. 17) the more energetically demanding it is to excite the electron population, whence the stopping cross section for a given series of films exhibits the same scaling behavior with layer number as the cohesive energy. Thus, $S(0, v)$ is the best (in the sense of physically consistent) estimator of $S_{crystal}(v)$ obtainable from a series of N -layer calculations, in correspondence with the estimator provided by \mathcal{E}_0 for the crystalline cohesive energy. Similarly, we may identify $S_L(v)$ as a consistent estimator of $S_{surf}(v)$ from N -layer calculations.

Strain-induced Derivative Discontinuities in Spin Moments

We conclude with a brief discussion of the relationship between strain and spin moment in the Fe 1-L.²² Much else has been published by other workers on Fe UTF's but here we focus only on that one issue. A series of spin-polarized LSDA calculations was performed on an Fe 1-L in hexagonal symmetry over a range of lattice constants $3.4 \leq a \leq 5.85$ au; from 5.0 au downward every 0.1 au was sampled. The spin moment as a function of a turns out to be remarkably rich in features: two discontinuities in slope (at 4.7 and 4.2 au) followed by collapse from a high-spin to low-spin state between the points at 3.7 and 3.6 au.

As discussed in Ref. 22 and Harrison's very insightful tight-binding analysis,²³ all these features are connected with the conversion of fully occupied bands (in the ferromagnetic regime) to partial occupancy and with the band-edge discontinuity in the DOS for systems with two-dimensional periodicity which we have already discussed for the Li UTF's. The band edge DOS in a crystal does not have that discontinuity, hence would yield a discontinuity only in $\partial^2 \mu / \partial a^2$, not in the first derivative of the moment. In concept we have come full circle to Schulte's argument!¹ At low lattice constant the system is paramagnetic, with four bands crossing E_F ,

while at $a = 5.85$ au only one majority-spin band crosses E_F and the system is ferromagnetic. As the system is expanded, therefore, a majority spin band narrows and falls with respect to E_F until it is entirely below, then the process repeats for the next two higher bands. In order (with respect to increasing a), the K_1 , $\Gamma_6^{(-)}$, and finally the M_2 band edges cross E_F . With respect to increasing a , the first crossing is the jump to the high-spin state, while the latter two correspond to flattening of the curve toward eventual saturation.

If they were to be found experimentally, these discontinuities in $\partial\mu/\partial a$ would be quite significant for understanding DFT and approximations thereto. The reason is that the physical quantity involved, the spin moment, is rigorously interpretable (from the electron spin density) in DFT. Similarly, the highest occupied Kohn-Sham eigenvalue is the only one with an exact interpretation: it is E_F for the case of exact K-S theory. Hence the quality of an approximation to DFT would be tested extremely stringently by the way in which the calculated spin moment behaved relative to the calculated E_F as a function of strain in comparison with experiment.

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